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We report polarized photoluminescence excitation spectroscopy of the negative trion in single charge-tunable InAs/GaAs quantum dots. The spectrum exhibits a *p*-shell resonance with polarized fine structure arising from the direct excitation of the electron spin triplet states. The energy splitting arises from the axially symmetric electron-hole exchange interaction. The magnitude and sign of the polarization are understood from the spin character of the triplet states and a small amount of quantum dot asymmetry, which mixes the wave functions through asymmetric *e-e* and *e-h* exchange interactions.

The spin state of a singly charged quantum dot (QD) could act as a bit of quantum information that is controlled and measured optically through the charged exciton (trion) [1]. Because the optical control of spin information depends profoundly on fine structure, selection rules, and spin interactions, there is considerable interest in high-resolution spectral studies of the trion [2]. The trion has been investigated using *nonresonant* excitation in single QDs [3–8], and, in particular, there have been many studies of the "singlet" trion, in which the two electrons are spin paired. One result of these studies is the demonstration that electron-hole exchange, which plays such an important role in the neutral exciton [9,10], is absent in the singlet trion [6,8]. However, in the trion's excited state, in which one of the electrons occupies the *p* shell, the two electrons can also form a spin triplet. In this case electron-electron (*e-e*) and electron-hole (*e-h*) interactions partly remove the high (eightfold) spin degeneracy, leading to fine structure in the excited state of the trion. Such structure due to spin in quantum dots has been discussed theoretically [11] and invoked to explain nonresonant negative photoluminescence (PL) polarization in InAs dots [12], quantum beating in InP dots at zero field [13], and splittings in multiexciton and multicharge PL lines in CdSe [3] and InAs [14] dots.

Here we measure *resonantly* the optical spectrum of a single electron in individual charge-tunable InAs/GaAs QDs for the first time using polarized PL excitation (PLE) spectroscopy. In this spectrum we discover a well-resolved doublet structure with a remarkable polarization reversal that we will assign to trion triplet states.

The InAs QDs were grown by molecular beam epitaxy using an indium flush technique [4,15]. The QDs were embedded in a Schottky diode to control their electronic charging [5,7]. The diode structure was grown on a (001) *n*-type GaAs substrate covered with a 500 nm thick GaAs

buffer layer (Te doped at $\sim 5 \times 10^{17}$ cm^{-3}), followed by 80 nm of GaAs, the InAs QDs, 230 nm GaAs, 40 nm Al$_{0.3}$Ga$_{0.7}$As, and a 10 nm thick GaAs cap. The PL was excited and detected at ~ 10 K through aluminum shadow masks with submicron apertures using a cw, Ti:sapphire laser (<7 μeV linewidth) and a 0.5 m spectrometer with a CCD. With voltage controlled retarders for polarization in a strictly backscattering geometry, we obtained polarization fidelity greater than 95% at the single dot level.

The charge state of individual QDs was controlled by adjusting the bias across the diode while monitoring the PL spectra. Typical bias dependent PL spectra for nonresonant excitation, $E_{\mathrm{exc}} = 2.3$ eV, are displayed in Fig. 1(a). The image shows the PL emission from both the *s* and *p* shells with ~ 50 meV energy separation between them. Electronic charging in discrete steps is clearly identifiable in the higher resolution *s*-shell spectra in Fig. 1(b) with excitation energy at $E_{\mathrm{exc}} = 1.44$ eV, just below the wetting layer energy. The bias at which the dot is charged with a single electron is identified by the appearance of the negative trion, X^- [4,14].

Low power PLE spectra in which the excitation energy is scanned through the energy range of the *p*-shell emission reveal intense resonances in the X^- with strong polarization dependence (Fig. 2). It is seen (dot B) that the PLE spectrum of the X^- is shifted down in energy relative to the X^0 and becomes strongly polarized when the dot is charged with a single electron. A future analysis of all features will require concepts suggested previously to account for the complex PLE spectrum of a neutral exciton [16,17], including strong phonon coupling [18], excited state mixing [19], forbidden transitions to the continuum [16,20,21], and splitting of the *p* shells.

In general, we find two very distinctive features. The first is a set of lower energy resonances that are strongly copolarized with the laser. In dot B this occurs at
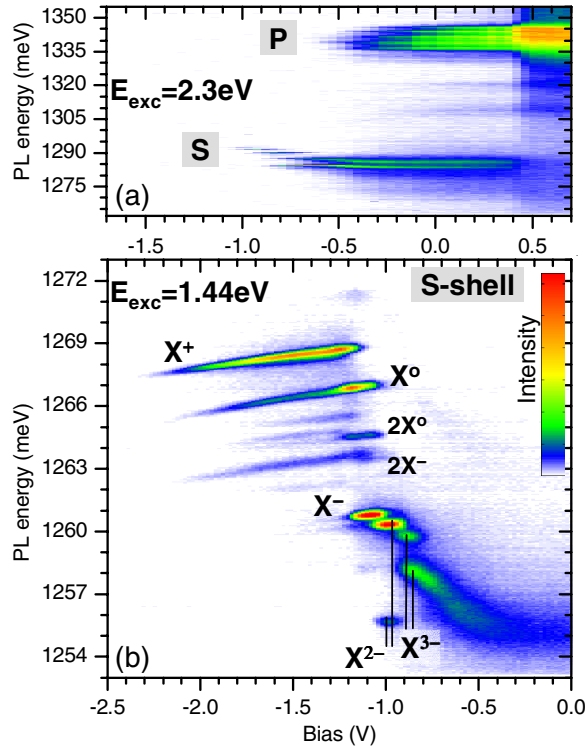
FIG. 1 (color online). Bias dependent PL intensity maps. (a) Emission from both the *s* and *p* shells of a single dot. (b) Charging structure of the *s*-shell emission from another dot.
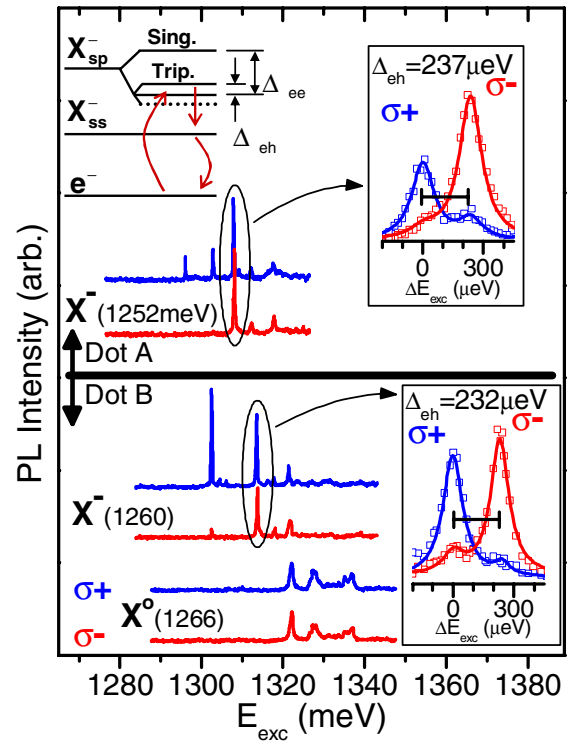

FIG. 2 (color online). Polarized PLE spectra of the X^- under σ^+ excitation for two dots. The PL emission energies are given in parentheses. The top (bottom) trace for each spectrum is for σ^+ (σ^-) PL detection. The polarized doublet for each dot is expanded in the insets. For dot B, the associated X^0 PLE spectrum is also displayed. The left inset shows the energy levels of the ground (X_{ss}^-) and excited (X_{sp}^-) state trions with and without *e-e* (Δ_{ee}) and *e-h* (Δ_{eh}) exchange splittings.

~ 1302 meV, which is 42 meV above the PL emission. We tentatively assign this structure to nominally forbidden transitions involving states with two *s*-shell electrons and an excited hole [22]. The second feature is a higher energy resonance (for dot B at ~ 1313 or ~ 53 meV above the PL) that displays a fine structure doublet well resolved in circular polarization. To date, we have investigated 9 QDs, all of which display this resonant doublet in the range between ~ 50–57 meV above the X^- PL energy with a splitting of ~ 216–237 μeV. We will develop an understanding of this doublet in what follows.

High-resolution PLE spectra of the doublet for the two circular PL polarizations are shown in the insets of Fig. 2. For all dots, both lines exhibit extremely large polarizations ranging from $\sim 65\%$ to greater than 95% calculated by $P = (I^+ - I^-)/(I^+ + I^-)$, with I^+ (I^-) representing the integrated intensity of the σ^+ (σ^-) polarized PLE resonance under σ^+ polarized excitation. The half-widths of each of the lines are ~ 50 μeV in the low power limit. In all the QDs the low-energy component is positively polarized, and the high-energy line is negatively polarized, i.e., parallel and antiparallel with the laser, respectively. In the following we argue that this PLE resonance and its polarized fine structure result from direct excitation into the *triplet states* of the excited trion (see Fig. 2, left inset).

In Fig. 3 we consider in more detail the optical excitation of an *e-h* pair directly into the *p* shell in the presence of an unpolarized "resident" *s*-shell electron [11]. The electrons

will form symmetric spin triplets and an antisymmetric spin singlet split by the *e-e* exchange of $\Delta_{ee} \approx 6$ meV [5]. The triplet states are further split by the axially symmetric part of the *e-h* exchange interaction (Δ_{eh}) into a set of three degenerate doublets with the order given in Fig. 3. This splitting is expected to be several hundred μeV as deduced from the transverse magnetic field dependence of the X^0 [6], and from the fine structure of the X^{2-} [14] and $2X^-$ lines [3,14]. In Fig. 3 the trion states have been sorted into two columns that show vertical optical transitions under circularly polarized excitation. Only four of the six triplet states are optically allowed. Thus, resonant σ^+ light should lead to excitation of two states split by Δ_{eh} (wavy "up" arrows in Fig. 3), as observed. These two transitions differ in the initial state by the spin projection of the resident electron, and thus the laser frequency and polarization provide a spin selective probe.

To understand the dramatic polarization reversal in the fine structure doublet, we consider relaxation from the excited trion *triplet* states (populated by σ^+ light) to the luminescing *s*-shell *singlet*. The relaxation of the low-energy $m_s = +3/2$ triplet state (left side of Fig. 3) conserves both the hole spin and the spin projection of the electrons. The low-energy resonance should therefore re-
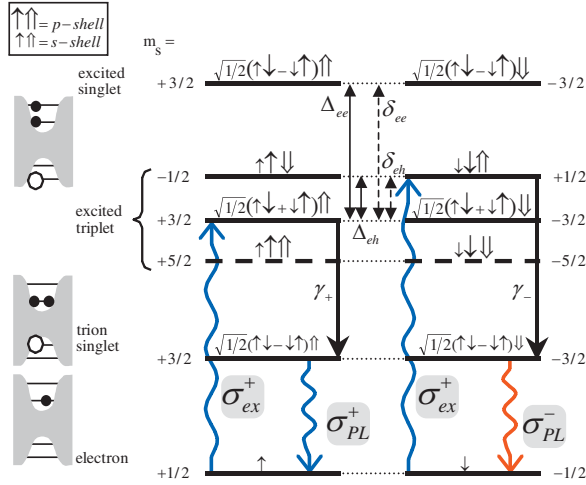
systematically

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(Fig. 3) [25]. The Dzyaloshinskii-Moriya form of this exchange, given by $\delta_{ee}(s_1 \times s_2)$, arises from spin orbit coupling [26,27] and can mix the triplet states of electrons with the corresponding *excited* singlet states, which relax quickly to the ground state singlets (within $\tau = 1$ ps). Using $\gamma_+ \approx (\delta_{ee}/\Delta_{ee})^2 \tau^{-1}$ to estimate the relaxation rate of the triplets, our results indicate that $\delta_{ee}/\Delta_{ee} \approx 1/5$. We have obtained the asymmetric exchange for a single dot within a Kane model calculation [27] and find a term $\delta_{ee}(s_1 \times s_2)_z$ that mixes the excited singlet and the triplet states if the potential has inversion asymmetries in the lateral directions. We have evaluated δ_{ee} for dots with modest cubic and fourth order terms added to the lateral parabolic potentials. The value $\delta_{ee}/\Delta_{ee} \approx 1/5$ is obtained with an anharmonicity of $\lesssim 12\%$ as seen in the spacing of the excited states. We believe this deviation from an ideal potential to be reasonable [28] and thus conclude that asymmetric *e-e* exchange can provide a channel for relaxation from triplet to ground state singlet.

Recently, negative PL polarization of the trion with *nonresonant* circularly polarized excitation was explained with two alternative models [12,29,30]. The first [29,30] is based on the creation and accumulation of dark excitons due to single spin flips of delocalized holes. Subsequent capture by a negatively charged QD and recombination leads to negative polarization. The second model [12] is based on the mutual *e-h* flip-flop transition mediated by the asymmetric *e-h* exchange in the triplet state. Recently, we proved [30] that the first mechanism dominates under nonresonant excitation in GaAs/Al$_x$Ga$_{1-x}$As QDs. Now, using polarized *resonant* excitation of the triplet states in InAs/GaAs QDs, where single carrier spin flips are suppressed, we have demonstrated directly the second mechanism for negative PL polarization.

In conclusion, we have discovered a fine structure doublet in the polarized PLE spectra of the negative trion. We show that the doublet arises from the resonant excitation of triplet states of the trion with splitting due to the symmetric *e-h* exchange interaction. Furthermore, the asymmetric part of the *e-h* exchange mixes the triplet states, while the asymmetric part of the *e-e* exchange mixes the excited singlet with the triplet states. This leads to two separate relaxation channels that are selected by laser energy and recombine with both positive and negative polarization. Finally, we note that because the components of the doublet arise from opposite spin states of the resident electron (Fig. 3), these polarized resonant transitions provide an all optical PLE method of selectively probing the spin state of a single electron confined in a QD.

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